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Investigation of the characteristics of DLC films on oxynitriding-treated ASP23 high speed steel by DC-pulsed PECVD process

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ABSTRACT

In this study, diamond-like carbon (DLC) films are coated onto oxynitriding-treated ASP23 high-speed steel by DC-pulsed PECVD. The main research parameters of the DC-pulsed PECVD process are the various duty cycles (5%, 10%, 15% and 20%) used to examine the coating characteristics. In order to investigate the DLC film properties, a Raman spectroscopy analysis, wear test, adhesion, and hardness tests are performed. The experimental results show that the duplex coating layers have optimal properties when DLC films are treated with a low-pulse voltage (−1.5 kV), a coating time of 90 min and duty cycles maintained at 10%. As a result, the DLC/oxynitriding duplex-treated specimens with the highest surface hardness ($Hv_{0.01}$ 1931) and the lowest wear volume loss (3×10^{-3} mm^3) can be acquired. In addition, compared with non-treated (polarization resistance $R_p = 5 \times 10^3$ Ω cm^2) and oxynitriding-treated ($R_p = 8 \times 10^3$ Ω cm^2) specimens, the optimal DLC/oxynitriding duplex-treated ASP23 high-speed steel possesses the lowest corrosion current ($I_{corr} = 8 \times 10^{-6}$ A cm^{-2}) and highest polarization resistance ($R_p = 1 \times 10^4$ Ω cm^2) in 3.5 wt.% NaCl solutions. This result confirms that the DLC/oxynitriding duplex treatment enhances optimal wear and corrosion resistance.

1. Introduction

ASP23 high speed steel is a chromium–molybdenum–tungsten–vanadium alloyed steel. The powder metallurgy manufacturing route used for ASP23 high speed steel provided a higher harden ability, better wear resistance, and excellent toughness. Consequently, coupled with its high hardness, good toughness and high temperature tempering, it means that ASP23 high speed steel is very suitable for surface coating treatments, in particular for PVD or CVD process [1–3].

Nitriding is a thermo-chemical treatment with nitrogen diffusion, which leads to increase the surface hardness of the treated steels. It shows an effective increase of thermal fatigue characteristics due to the effects of compressive stress and the hardened surface [4,5]. In addition, most steels can form several kinds of oxides (Fe_2O_3 and Fe_3O_4) during the oxidation process. The complex oxide layer of Fe_2O_3 and Fe_3O_4 structures possessed a passive film and formed on the surface, which improves the corrosion and erosion properties of the steel [6,7]. Our previous studies found that oxynitriding specimens could form the passive oxidative film and high hardness, which contributed a better mechanical property during the duplex coating treatments [5–7].

Diamond-like carbon (DLC) films have excellent properties such as high hardness, low friction, and chemical inertness. Thus, the film is suitable for coatings, and much of works have been carried out on the preparation of the films by means of physical vapor deposition (PVD) and chemical vapor deposition (CVD) [8,9]. Furthermore, direct current pulsed (DC-pulsed) plasma-enhanced chemical vapor deposition (PECVD) is one of the most promising methods for surface modification of dies and tools used in various industries. Generally speaking, PECVD can be either RF (radio frequency) or DC powered, with each having certain advantages and disadvantages [10,11]. Recently, attention was paid to PECVD of DLC films. Moreover, RF and DC-pulsed plasma sources were applied for film deposition. The DC-pulsed PECVD technique enables the uniform coating of complex-shaped 3D parts like forming tools, because of the plasma activation of the gas phase, and lowers the deposition temperature significantly as compared to conventional thermal CVD [12,13]. In addition, many previous experimental results suggest that plasma CVD using DC-pulsed discharge could be effective in improving the adhesion, where specimens on the substrate can be controlled by the conditions of the pulse bias [9,14,15].

A surface treatment is often used to increase wear resistance, as well as to improve surface hardness and tool life [16]. In this study, the oxynitriding process used steam at the end of the nitriding stage as an oxidizing medium; this was an integral part of the surface treatment. Furthermore, plasma CVD using a DC-pulsed discharge has proved to be effective in improving the adhesion and other properties of the

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coating films. Therefore, the DLC/oxynitriding duplex treatment utilized a DC-pulsed PECVD process coated onto an oxynitriding-treated specimen of ASP23 high-speed steel in order to study the characteristics of DLC films, as well as to increase tool life.

2. Experimental procedure

In this study, ASP23 high-speed steel was chosen as the substrate material to undergo a homogeneous heat treatment: it was quenched at 1180 °C and tempered at 550 °C for 3 h; this was repeated 3 times to reach a hardness of 65 ± 1 HRC. Furthermore, a typical microstructure was obtained through commercial heat treatment, comprising the structure of tempered martensite and various metallic carbides. The chemical compositions (mass %) of ASP23 high-speed steel are as follows: 1.28% C, 4.0% Cr, 5.0% Mo, 6.4% W, 3.1% V and 80.22% Fe. The oxynitriding-treated specimens of ASP23 high-speed steel were nitriding-treated for 6 h at 550 °C and oxidized via steam for 45 min at 525 °C.

In the DLC/oxynitriding duplex treatments, in which oxynitriding treatment was the same as in the abovementioned process, oxynitriding specimens underwent DLC coating using DC-pulsed PECVD technology, as shown in Fig. 1. In this study, the DC-pulsed PECVD utilized a unipolar negative-pulsed voltage. After the chamber was pre-evacuated air by using a rotary pump, a CH_4 mixture of gas was supplied to the chamber. In addition, to study the effects of the different duty cycles on the DC-pulsed plasma CVD process, the various duty cycles included 5%, 10%, 15% and 20%. For example, the 5% duty cycle means that the plasma deposition time is only with 5 μs during the 100 μs. Simultaneously, the coating times of the DC-pulsed PECVD were maintained at 90 min; the pulsed voltage and frequency were kept at −1.5 kV and 10 kHz, respectively. Moreover, CH_4 gas (5 sccm) was added at less than 10^{-2} Torr and continued for 90 min, followed by depositing of the DLC films.

The aim of this study was to investigate the characteristics of DLC films by using different duty cycles for the DC-pulsed PECVD treatments. In order to evaluate the properties of DLC films and tribological behaviors for DLC/oxynitriding treated ASP23 high speed steel, the Raman spectroscopy analysis (Horiba MOF-iHR550), wear test (POD-FM406), roughness test (ET4000A), indentation test (Indentec-8150LK) [13], scratch tests (ASTM C1624-5, JLST022 Scratch Tester J & L Tech. Co., Korea), XRD (Rigaku DMX-2000) and SEM (Hitachi-S4700) microstructure inspections were performed. The wear resistance of the specimens was evaluated in a ball-on-disk test (ASTM G99). The wear test parameters were as follows: the specimen size was Ø36 × D5 mm, the diameter of WC ball (HRA 90 ± 1) was 6 mm, axial load was 2 N, disk rotation was 200 rpm, sliding speed was 0.63 ms^{-1} and total rotation was 10,000 revolutions.

In addition, corrosion potential analysis uses three electrodes method and is followed by ASTM G59-97: the reference electrode is saturated with silver–silver chloride electrode, auxiliary electrode uses a platinum electrode, and the working electrode is connected to the test specimens [12]. The contact area of the specimen was 2.01 cm^2. The corrosive solvent used 3.5 wt.% NaCl maintained at room temperature. A scanning speed of 0.01 Vs^{-1}, an initial potential of −1.0 V, and the final potential of 1.0 V were controlled. The polarization curve was obtained by Corr-View software to analyze and compare the corrosion potential (E_{corr}), corrosion current (I_{corr}) and polarization resistance (R_p) of various surface treatments.

3. Results and discussion

3.1. Effects of oxynitriding-treated ASP23 high-speed steel

Fig. 2 shows the XRD patterns and surface hardness of the oxynitriding-treated ASP23 high-speed steel. The primary structures of the oxynitriding layer were Fe_3O_4, Fe_3N (ε phase) and Fe_4N (γ′ phase), as shown in Fig. 2a. Moreover, Fe was the main matrix element for the ASP23 high-speed steel, which appeared in the XRD patterns. This result also demonstrated that ASP23 high-speed steel, successfully nitride-treated at 550 °C for 6 h and oxide-treated at 525 °C for 45 min, possessed a well-oxidized layer and crystal properties. The surface hardness curve of the oxynitriding-treated ASP23 high-speed steel is shown in Fig. 2b. The depth of the surface-hardened layer was about 60 μm, and the diffusion layer was less than 200 μm via the oxynitriding treatment. The surface hardness of the ASP23 high-speed steel was increased to $Hv_{0.05}$ 1280 after the oxynitriding treatment. Significantly, the complex oxide layers of the Fe_3O_4 and nitride structures (Fe_3N, Fe_4N) were also formed on the surface, which improved the surface hardness of the steel. Generally, the Fe_3N and Fe_4N layers are effective in reducing the mobility of dislocation, which leads to increased hardness. Therefore, it is reasonable to suggest that the surface area has a higher concentration of nitrogen ions,

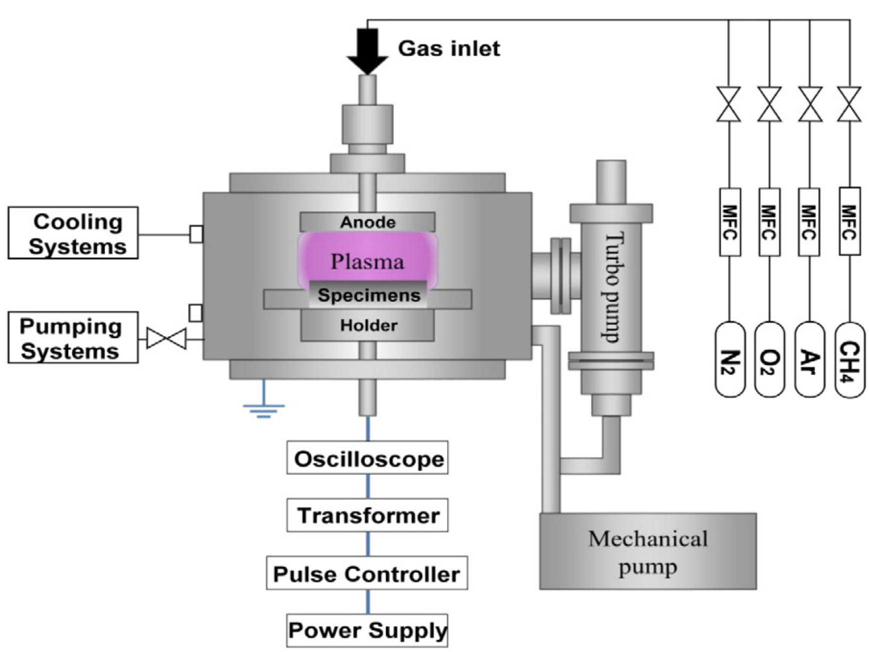

Fig. 1. Schematic of the DC-pulsed PECVD system.